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EXOTHERMIC CYCLIC PEROXIDE REACTIONS. DECOMPOSITION OF A 1,2,4---ETC(U)
MAY 77 G B SCHUSTER, L A BRYANT

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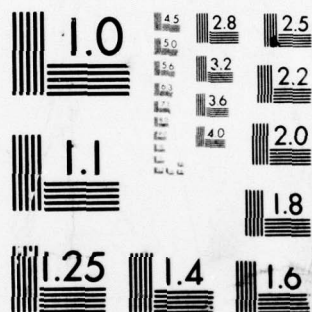
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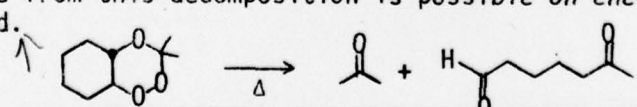
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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Thermolysis of trioxane in degassed octane solution resulted in the formation of acetone and adipaldehyde. The reaction was shown to be uni-molecular with a free energy of activation of 39 kcal/mole. Although chemi-luminescence from this decomposition is possible on energetic grounds, none was detected.  | | |

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* Trans 4-4-dimethyl-2-3-5-trioxabicyclo-4-4-0-decane

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TECHNICAL REPORT NO. N0014-76-C-0745-05

Exothermic Cyclic Peroxide Reactions.

Decomposition of a 1,2,4-Trioxane.

by

Gary B. Schuster and Lynn A. Bryant

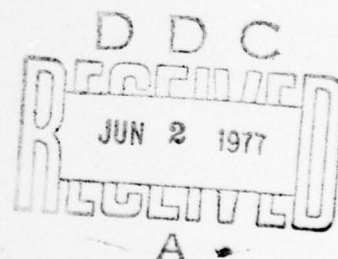
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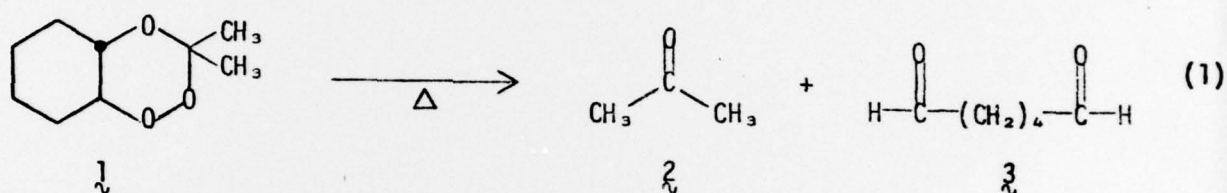
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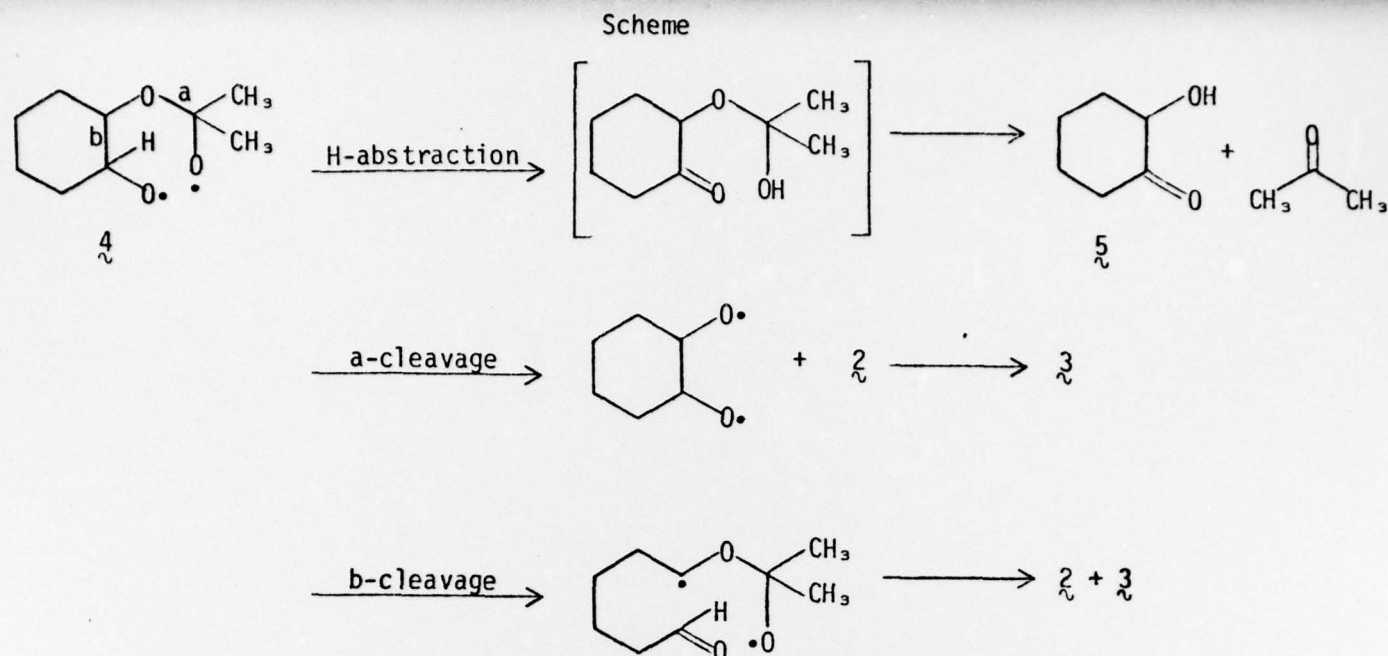
Recent reports on the thermolysis of cyclic peroxides^{1,2} and the suggestion that the cyclic as-trioxane ring may be a key chemiluminescent intermediate³ prompt us to communicate our results on the thermolysis of trans-4,4-dimethyl-2,3,5-trioxabicyclo[4.4.0]decane (**1**).



Peroxide **1** was prepared by the procedure of Payne⁴ from cyclohexene, acetone and hydrogen peroxide. Purification was accomplished by repeated crystallization from pentane followed by distillation at reduced pressure to yield analytically pure peroxide. Analysis of the 220 MHz proton nmr spectrum of **1** revealed the ring junction to be trans⁵.

Degassed solutions of peroxide **1** in octane or diphenyl ether were thermolyzed at temperatures ranging from 189°C to 160°C. Analysis of the resulting product mixture by mass and nmr spectroscopy and gas chromatography revealed acetone (**2**) and adipaldehyde (**3**). The yield of acetone was essentially quantitative, however, the amount of aldehyde **3** formed was dependent upon the extent of reaction. Extrapolation to very low conversion indicated that the adipaldehyde was formed in ca. 95% yield. Independent control experiments confirmed that aldehyde **3** was unstable under the reaction conditions.

Investigation of the kinetics for the decomposition of peroxide **1** indicated that the rate of reaction was cleanly first order in peroxide concentration for at least four



A second common reaction of alkoxy radicals is α -cleavage to form carbonyl compounds. Biradical **4** must break two α -bonds to form the observed products. Three choices for the sequence of bond breaking steps from this intermediate seem apparent. First, if the bond labeled a (Scheme) cleaves first, acetone and a 1,4-biradical will be formed. It should be noted that this 1,4-biradical is the anticipated intermediate in the chemiluminescence of the corresponding 1,2-dioxetane.⁷ Alternatively, initial cleavage of the bond labeled b would generate the 1,4-biradical resulting from the as yet unknown 1,3-dioxetane ring system. Finally, bonds a and b could cleave simultaneously generating the observed products in one step from the 1,6-biradical. Our results cannot distinguish between these possible reaction pathways.

Peroxide **1** is potentially a chemiluminescent intermediate.³ Group equivalent calculations⁸ indicate that the reaction of **1** to **2** and **3** is exothermic by ca. 37 kcal/mole. Inclusion of the observed activation energy suggests that ca. 77 kcal/mole is available for the formation of electronically excited states. This quantity is sufficient to populate the triplet state of acetone. Unfortunately, the high temperatures necessary to decompose peroxide **1** interferes with the luminescent process. No chemiluminescence was observed during reactions of **1**.

In summary, we have observed that upon thermolysis the relatively stable cyclic peroxide **1** undergoes unimolecular cleavage to form carbonyl compounds **2** and **3** with high efficiency. In addition, the suspected intermediate biradical formed from homolysis of the oxygen-oxygen bond must rearrange rapidly (most probably) by an α -cleavage reaction. Finally, no

chemiluminescence was observed during this reaction although sufficient energy is available to form the lowest triplet state of the observed products.

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